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Thermodynamics of High-Temperature High-Pressure Solutions.

Argon in Molten Sodium Nitrate¹

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The solubility of Ar in molten NaNO_3 has been determined over a temperature range from 356 to 441° at pressures from 151 to 395 atm. Henry's law constants, K_h , and distribution coefficients, K_e , were found for the resulting six solubility-pressure isotherms. A plot of $\log K_h$ vs. $1/T$ yielded a value for the enthalpy of solution, ΔH , of -1.69 ± 0.21 kcal mole⁻¹. The standard entropy of solution, corresponding to a standard state of 1 *M* concentrations of gas in both the liquid and gaseous states, ΔS_e° , resulted as -4.97 ± 0.32 eu from the intercept of a plot of $\log K_e$ vs. $1/T$. The results are compared to similar work in this laboratory involving N_2 in fused NaNO_3 , where $\Delta H = -2.73 \pm 0.09$ kcal mol⁻¹ and $\Delta S_e^\circ = -6.78 \pm 0.18$ eu, and with low pressure work in molten fluoride systems performed in other laboratories where ΔH values were endothermic. Calculations of ΔH 's of solution for both the Ar and N_2 work using approximate fugacities rather than pressures did not change the values appreciably, yielding -1.84 ± 0.21 kcal mol⁻¹ for Ar in NaNO_3 and -2.69 ± 0.08 kcal mol⁻¹ for N_2 in NaNO_3 . Conclusions are drawn which compare the relative contributions of exothermic solvation effects and endothermic molecular cavity creation work in the liquid to the over-all heat of solution. It is seen that predictions based on such a simple model conceived for the N_2 work are, for the most part, reasonably confirmed in the present investigation.

Introduction

In a previous paper the authors reported the results of a study of the temperature and high-pressure dependences of the solubility of N_2 in fused NaNO_3 .² The system was found to possess an exothermic heat

of solution and a rather high negative entropy of solution. A tentative simple model was advanced which

(1) This work was presented in part at the Third Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 1967.

conceived of exothermic solvation effects dominating over endothermic work of molecular cavity creation necessary to accommodate a solute particle. It was predicted that a molecule of comparable size to N_2 , but of less polarizability, such as Ar, should therefore be somewhat less soluble in $NaNO_3$ than is N_2 , and should have a somewhat less exothermic heat of solution (if indeed exothermic at all). In addition, a monatomic gas, such as Ar, would be expected to suffer a less negative entropy of solution than did the diatomic N_2 molecules. The present investigation serves to confirm these predictions to a large degree.

Experimental Section and Data Treatment

The apparatus and procedure were the same as previously described.² Four separate runs were completed, each at salt temperatures of 714, 701, 679.5, 663, 642, and 629°K to yield six solubility–pressure isotherms consisting of four points apiece. The maximum Ar pressure for any experiment was 395 atm, and the minimum pressure was 151 atm for any run.

As in previous work,^{2,3} the decrease in moles of the gas phase in the system, between a given high temperature and room temperature, was attributed to gas solubility in the melt. The density of liquid $NaNO_3$, $d_{t,p}$, at a given centigrade temperature, t , and piston pressure, P (atm), used for calculating the total volume of pure salt was obtained from the empirical equation

$$d_{t,p} = 2.134 - (7.03 \times 10^{-4})t + (3.9 \times 10^{-5})P \text{ g cm}^{-3} \quad (1)$$

where the temperature coefficient is from the work of Bloom, Knaggs, Molloy, and Welch,⁴ and the pressure coefficient is based on the data of Owens.⁵ An error, which should be well within the experimental error of the over-all procedure, probably persists as the result of using such pure-salt densities as estimates of the actual solution densities.

At the higher temperatures and pressures employed in this work (much above 600°K and 200 atm), use of the best P – \bar{V} – T data available (those compiled by Din⁶) would entail too extensive extrapolations for reasonably accurate estimates of the molar volumes of Ar. Therefore, the Beattie–Bridgeman equation was employed to find \bar{V} at all temperatures and pressures used, for consistency. This equation is usually a quartic in \bar{V} ⁷

$$0 = P\bar{V}^4 - RT\bar{V}^3 - (RTB_0 - Rc/T^2 - A_0)\bar{V}^2 + (RcB_0/T^2 - aA_0)\bar{V} - RcB_0/T^2 \quad (2)$$

However, with numerical values for the constants for Ar of:⁸ $A_0 = 1.2907$, $a = 0.02328$, $B_0 = 0.03931$, $b = 0$, and $c = 5.99 \times 10^4$, the equation reduces to a cubic in \bar{V} for Ar since $b = 0$

$$f(\bar{V}) = P\bar{V}^3 - RT\bar{V}^2 - (RTB_0 - Rc/T^2 - A_0)\bar{V} + (RcB_0/T^2 - aA_0) = 0 \quad (3)$$

\bar{V} (in l. mole⁻¹) was found for every P – T pair employed in this work by programming an IBM-1410 to calculate \bar{V} from eq 3 by the Newton–Raphson method. Ideal gas values for \bar{V} were used as beginning trial values. Generally, only four iterations were required by the computer to produce an acceptable value of \bar{V} , but in a very few cases five such iterations were necessary. (An acceptable value of \bar{V} was taken to have been attained when the absolute value of $[f(\bar{V})/(df(\bar{V})/d\bar{V})]/\bar{V}$ was less than 10^{-5} .) To test the accuracy of solutions so obtained for the high-temperature and pressure region, some calculated \bar{V} values were compared to Din's literature values⁶ at the upper end of his table. Table I compares these calculated \bar{V}

Table I: Comparison of Some \bar{V}_{lit} ⁶ and \bar{V}_{calc} Values for Argon Obtained by Computer Solutions of the Beattie–Bridgeman Equation

P , atm	T , °K	\bar{V}_{calc} , l. mole ⁻¹	\bar{V}_{lit} , l. mole ⁻¹	% diff
180	550	0.2630	0.2622	0.305
180	600	0.2877	0.2864	0.454
200	550	0.2381	0.2371	0.422
200	600	0.2605	0.2590	0.580

quantities with their corresponding literature values. It is seen from this table that the agreement of the \bar{V} values is good. We assumed, therefore, that the Beattie–Bridgeman calculations of \bar{V} for Ar would satisfy our needs in this work.

Average Henry's law constants, K_h , and distribution coefficients, K_c , where

$$K_h = C_d/P \text{ mol of gas cm}^{-3} \text{ atm}^{-1} \quad (4a)$$

$$K_c = C_d/C_g \text{ (unitless)} \quad (4b)$$

(C_d = concentration of gas in dissolved phase, C_g = concentration of gas in gaseous phase) were calculated for each solubility–pressure isotherm.

Results

Table II summarizes the experimental temperatures, pressures, solubilities, Henry's law constants, and distribution coefficients. Theoretical values of the latter

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